SYNTHESIS OF HETEROATOMIC ORGANOSULFUR DERIVATIVES AND THEIR RESPONSE TOWARDS Ag(I), Zn(II), Cd(II) AND Hg(II) IONS

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by

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Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the

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Dedicated

to

My Beloved parents

Certificate

This is to certify that the thesis entitled, ***"Synthesis of Heteroatomic Organosulfur derivatives and Their Response Towards Ag(I), Zn(II), Cd(II) and Hg(II) ions"*** *being submitted by* ***Mr. Anuj Kumar Baliyan,*** *to the* ***Indian Institute of Technology Delhi*** *for the award of degree of '****Doctor of Philosophy'*** *in Chemistry is a bonafide research work carried out by him. Mr. Anuj Kumar Baliyan has worked under my guidance and supervision and has fulfilled the requirements for the submission of thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis have not been submitted in part or in full, to any other University or Institute for award of any degree or diploma.*

Date:

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ABSTRACT

The thesis entitled "**Synthesis of Heteroatomic Organosulfur Derivatives and Their Response Towards Ag(I), Zn(II), Cd(II) and Hg(II) Ions**" describes the design and synthesis of heteroatomic organochalcogen derivatives and their structural aspects with d^{10} metal ions.

Chapter I presents a brief overview on heteroatomic organochalcogen based donors and their coordination chemistry with group 12 metal ions and to view their potential applications in various fields such as supramolecular chemistry, cation and anion sensing, catalysis and biological sciences.

Chapter II describes general synthetic approach with experimental details which used for the preparation of precursors in the current research work. The brief description of instruments and several techniques which were used for the analysis of the novel synthesized precursors and compounds is also described in this chapter.

Chapter III describes the design and Synthesis of bis-(heteroarylthio)methane and bis-(arylthio)methane based donors. As a part of current investigation to understand the behaviour of heteroatomic organic donor molecules, especially bis(2-pyridylthioether) methane is one of the simplest example of such derivatives bearing N and S donor centres. The chemistry of bis(2-pyridylthioether)methane with the view that on their appropriate Metal-Ligand (M:L) combinations and their coordination behaviour specially towards with Zn^{2+}, Cd^{2+} and Hg^{2+} ions. A comparative structural study specifies the influence of relativistic effect in mercury complexes.

Chapter IV describes the design and synthesis of arylthio and arylthiomethyl based dipodal ligands with ethylene spacer. An additional carbon centre to enhance the flexibility at species

and bearing the presence of N and S donors show affinity towards d^{10} {Zn (II), Cd (II), Hg(II) and Ag(I)} metals. The formation of different types of metallosupramolecular assembly was deduced by various type of coordination possibility of these ligands with metals. To conclude other outcomes of this chapter with crucial role of anion to form the different type of assembly and solvents aspects is also observed in the result.

Chapter V describes the design and synthesis of three types of trifunctional organothioether derivatives. Due to inherent flexibility of the tripodal species various supramolecular assemblies were obtained with $AgNO_3$. Besides this, the solution state studies (absorption and emission studies) revealed that these species have high affinity for thiophillic metal ions Ag(I) and Hg(II) which can be attributed to the prominent role played by sulfur centres of these systems and very selectively bind with Ag(I) metal ion and may work efficient sensor for silver metal.

Chapter VI describes the design and synthesis of sulfur and selenium containing tripodal carboxamide. Interestingly, the coordination behaviour through hydrogen bonding was studied and identified as these amide containing molecules with different chalcogen (S and Se) atoms can selectively sense the nitrate (NO_3^-) anion. The physiochemical and solution state studies revealed that the nitrate (NO_3^-) anion is more interactive than other competitive anions such as bromide (Br^-), perchlorate (ClO_4^-) and hexafluoro phosphate (PF_6^-). Based on the results obtained one can conclude that the tripodal carboxamide systems are well suited for the recognition of anions with trigonal planar geometry in particular, nitrate which can be rationalized on the basis of the binding pattern of these tripodal systems.

सारांश

शोध प्रबंध ''सिंथेसिस ऑफ़ हेट्रोएटॉमिक ओर्गनोसल्फर डेरिवेटिव्स एंड देयर रेस्पॉन्स टुवर्ड्स Ag(I), Zn(II), Cd(II) एंड Hg(II) आयन्स'' हेट्रोएटॉमिक ऑर्गेनोक्लेकोजेन डेरिवेटिव के डिज़ाइन और संश्लेषण और d^{10} धातु आयनों के साथ उनके संरचनात्मक पहलुओं का वर्णन करते हैं।

अध्याय I, हेट्रोएटॉमिक ऑर्गेनोक्लेकोजेन आधारित डोनर्स पर एक संक्षिप्त अवलोकन और समूह 12 के धातु आयनों के साथ उनके समन्वय के रसायन को प्रस्तुत करता है और सुपरामौलेक्युलर केमिस्ट्री, कैटायन (धनायन) और अनायन (ऋणायन) संवेदी, कटैलिसीस(उत्प्रेरण) और जैविक विज्ञान जैसे विभिन्न क्षेत्रों में उनके संभावित अनुप्रयोगों को देखने के लिए।

अध्याय II, प्रायोगिक विवरण के साथ सामान्य सिंथेटिक दृष्टिकोण का वर्णन करता है जो वर्तमान अनुसंधान कार्य में पूर्ववर्ती तैयार करने के लिए उपयोग किया जाता था। इस अध्याय में नए संश्लेषित पूर्ववर्तियों और यौगिकों के विश्लेषण के लिए उपयोग किए गए उपकरणों और तकनीकों का संक्षिप्त वर्णन भी किया गया है।

अध्याय III में बिस-(हेटेरोएरायलथिओ)मीथेन और बिस-(एरायलथिओ)मीथेन आधारित डोनर्स के डिजाइन और संश्लेषण का वर्णन किया गया है। हेट्रोएटॉमिक आर्गेनिक डोनर अणुओं के व्यवहार को समझने के लिए वर्तमान जांच के एक भाग के रूप में, विशेष रूप से बिस-(2-पीरिडीलथिओईथर)मीथेन N और S डोनर केंद्रों के असर वाले ऐसे डेरिवेटिव्स का सबसे सरल

उदाहरण है। बिस-(2-पीरिडीलथिओईथर)मीथेन की रसायनिक दृश्य के अनुसार उनके उचित धातु-लिगेंड (M:L) संयोजन और विशेष रूप से Zn^{2+}, Cd^{2+} और Hg^{2+} आयनों के साथ उनके समन्वय व्यवहार। एक तुलनात्मक संरचनात्मक अध्ययन में मरकरी कॉम्पलेक्सेस में रिलेटिविस्टिक प्रभाव का वर्चस्व है।

अध्याय IV ऐरायलथिओ और ऐरायलथिओमिथाइल आधारित डाइपोडल लिगैंड्स के एथलीन स्पेसर के डिजाइन और संश्लेषण का वर्णन करता है। स्पीशीज में नम्यता को बढ़ाने के लिए एक अतिरिक्त कार्बन सेंटर और N व S डोनर की मौजूदगी तथा d^{10} {Zn(II), Cd(II), Hg(II) और Ag(I)} धातुओं के प्रति आकर्षण दिखाता है। धातुओं के साथ इन प्रकार के लिगैंड्स की भिन्न प्रकार की समन्वय संभावनाओं द्वारा विभिन्न प्रकार के मेटलोसुपरामॉलिक्यूलर असेंबली का गठन किया गया था। इस अध्याय के अन्य परिणामों को निष्कर्ष निकालने के लिए आयनों की महत्वपूर्ण भूमिका के साथ विभिन्न प्रकार के असेंबली और सॉल्वैंट्स पहलुओं को भी परिणाम में देखा जाता है।

अध्याय V तीन प्रकार के ट्राईफंक्शनल ओर्गनोथिओईथर डेरिवेटिव के डिजाइन और संश्लेषण का वर्णन करता है। ट्राईपोडल स्पीशीज में निहित नम्यता के कारण विभिन्न सुपरामॉलिक्यूलर असेम्ब्लीज़ $AgNO_3$ से प्राप्त हुई। इसके अलावा, सोल्युशन स्टेट अध्ययन (अवशोषण और उत्सर्जन अध्ययन) से पता चला है कि इन स्पीशीज के थियोफिलिक धातु आयनों Ag(I) और

Hg(II) के लिए उच्च आकर्षण है जो इन स्पीशीज के सल्फर केंद्रों द्वारा निभाई गई प्रमुख भूमिका के लिए जिम्मेदार ठहराया जा सकता है, बहुत चयनात्मक Ag(I) धातु आयन के साथ बाध्य होते हैं और सिल्वर धातु के लिए योग्य सेंसर (संवेदक) का काम कर सकते हैं।

अध्याय VI में सल्फर और सेलेनियम के ट्राईपोडल कार्बोक्सामाइड के डिजाइन और संश्लेषण का वर्णन हैं। दिलचस्प बात यह है कि, हाइड्रोजन बंधन के माध्यम से समन्वय व्यवहार का अध्ययन किया गया था और इन एमाइड के रूप में पहचान की गई थी जिसमें अलग-अलग क्लेकोजेन (S और Se) एटम वाले मॉलेक्यूल शामिल थे जो नाइट्रेट (NO_3^-) आयनों को चुनिंदा समझ सकते हैं। फिजियोकेमिकल और सोल्यूशन स्टेट स्टडीज से पता चला है कि नाइट्रेट (NO_3^-) आयन व अन्य प्रतिस्पर्धात्मक आयनों जैसे कि ब्रोमाइड (Br^-), परक्लोरेट (ClO_4^-) और हेक्साफ्लोरोफॉस्फेट (PF_6^-) से अधिक इंटरेक्टिव है। प्राप्त परिणामों के आधार पर यह निष्कर्ष निकल सकता है कि ट्राईपोडल कार्बोक्सामाइड सिस्टम विशेष रूप से त्रिकोणीय प्लैनर ज्यामिति के साथ आयनों की पहचान के लिए अनुकूल हैं, नाइट्रेट जो इन ट्राईपोडल सिस्टम के बंधन प्रतिमान के आधार पर तर्कसंगत हो सकते हैं।

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Abbreviation used

s	singlet
d	doublet
t	triplet
m	multiplet
br	broad
J	coupling constant
ppm	parts per million
Hz	hertz
MHz	mega hertz
r.t.	room temperature
hr	hour
min	minute
Ar	aryl
m.p.	melting point
Equiv.	Equivalent
THF	Tetrahydrofuran
DMF	Dimethyl formamide
DMSO	Dimethyl sulfonyl oxide